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ELECTRON DIFFRACTION

1927-1977

Electron Diffraction 1927–1977

Invited and contributed papers from the International Conference on Electron Diffraction held in London, 19–21 September 1977

Edited by P J Dobson, J B Pendry and C J Humphreys

Conference Series Number 41

The Institute of Physics
Bristol and London

CODEN IPHSAC 41 1–442 (1978)

British Library Cataloguing in Publication Data

International Conference on Electron Diffraction, London, 1977
Electron diffraction, 1927–1977 (Institute of Physics, Conference Series; No. 41; 0305-2346)
1. Electrons, Diffraction, Congresses
I. Title II. Dobson, P J III. Pendry, John Brian IV. Humphreys, Colin John V. Series
548′.83 QC793.5.E628

ISBN 0-85498-132-2

The International Conference on Electron Diffraction was organised by The Institute of Physics in collaboration with the Royal Microscopical Society and the Faraday Division of The Chemical Society under the sponsorship of the International Union of Crystallography, and the Royal Society

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Published by The Institute of Physics, Techno House, Redcliffe Way, Bristol BS1 6NX and 47 Belgrave Square, London SW1X 8QX in association with the American Institute of Physics, 335 East 45th Street, New York, NY 10017, USA.

Printed in Great Britain by Adlard and Son Ltd, Dorking, Surrey.

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Preface

The diffraction of electrons by solids was reported by two different groups early in 1927, both in letters to *Nature*. The first letter, that by C H Davisson and L H Germer (3 March 1927), showed diffraction peaks from a single crystal of nickel, using approximately 100 eV electrons. The second, by G P Thomson and A Reid (24 May 1927), reported Debye–Scherrer rings in the transmission of approximately 20 keV electrons through a thin film of celluloid; they also reported that the whole diffraction pattern was deflected by a magnet. This preliminary publication was followed by papers on the transmission patterns from a number of different metal foils and the verification of the de Broglie relation at a series of different accelerating voltages. A very significant, if less fundamental, effect was found in work started by S Nishikawa and S Kikuchi (*Nature* **121** 1019, 1928) on the transmission of 'fast' electrons through mica – what is now normally referred to as Kikuchi lines and bands.

The interval between the publication of de Broglie's thesis in 1924 and the start of experimental investigations in 1926 is noteworthy for a remarkable letter published in *Naturwissenschaften* by W Elsasser (15 July 1925). In this, it is pointed out that diffraction effects could account both for the Ramsauer effect and also for scattering peaks in the work of Davisson and Kunsman. It also pointed out that these scattering peaks fitted the de Broglie relation within a factor of two. It is a curious fact that no notice seems to have been taken of the Elsasser letter, and that in particular it had no influence on the work of either Davisson or G P Thomson.

It is particularly appropriate that the 50th anniversary of the discovery of electron diffraction should be marked by a conference in the Physics Department of Imperial College. G P Thomson was head of the department from 1930–52, and the electron diffraction group founded by him forms part of the department.

M Blackman
Conference Chairman

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The dynamical theory of electron diffraction

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Abstract. A few of the central themes of the dynamical theory of electron diffraction are surveyed including the optical potential, the concepts of Bloch waves and the dispersion surface, and the application of coupled plane-wave formulations to problems of x-ray production and backscattering in crystals.

1. Introduction

The discovery of electron diffraction fifty years ago directly confirmed the wave nature of the electron. It also revealed a new probe for the study of the structure of matter, uniquely sensitive to electric and magnetic fields and thus able to be easily focused and to be appreciably scattered by quite small numbers of atoms. However, these properties imply that in most solid samples a multiple scattering theory is required to interpret the results. The central role of dynamical theory in electron diffraction can thus be explained, but because of various practical difficulties which had to be overcome this position has been achieved only in the last two decades. At the present time the dynamical theory is being profitably and quantitatively applied to the interpretation and illumination of experimental data over an enormous field, covering the whole energy range from electron accelerators and high-voltage microscopes on the one hand to LEED and solid state band theory on the other. Detailed reviews of most of these fields have already been written and some of them are thoroughly surveyed elsewhere in these proceedings. To produce a full account of the development of dynamical theory, involving its interaction with experimental physics including both instrumental and computational technology, would be an interesting project for the historian of science but is impossible in the present context. It seems more appropriate to select for discussion a few of the central and unifying themes which are of current interest, in the hope that the ideas and techniques of dynamical theory developed for use in one field of application may sometimes be of value in another.

2. The optical potential in electron diffraction

To the extent that most scattering problems in both perfect and imperfect crystals have been reduced by modern computing power to the diagonalisation of enormous matrices or the solution of large sets of coupled differential equations, it can be argued that most of the essential physics now resides in the definition of the optical potential. Various aspects of this, including the history of its development which will not be repeated here, have been described by Kambe and Molière (1970), Dederichs (1972) and Howie and Stern (1972).

Most attention has been paid to the imaginary part of the potential, characterised in a crystal by Fourier coefficients $V_0^i = 2\Lambda/\hbar v$ describing the background absorption and mean free path Λ of electrons of velocity v, and V_g^i describing the anomalous absorption or Borrmann effect. These parameters were introduced on a semi-empirical basis in transmission electron microscopy and diffraction (Honjo and Mihama 1954, Kohra and Watanabe 1961, Hashimoto *et al* 1960, 1962, Lehmpfuhl and Molière 1961, 1962) and also in LEED (Duke and Tucker 1969, Jones and Strozier 1969, Pendry 1969). A theoretical basis for the concept was provided by Yoshioka (1957) who considered the contribution of single-electron excitations. This approach, subsequently developed by Whelan (1965) is satisfactory for the computation of $(V_g^i)_{el}$ (which is the electronic contribution to V_g^i) but this is found to be very small. To calculate the contribution $(V_0^i)_{el}$ it is essential to take account of collective excitations, such as plasmons, for which the complex dielectric constant $\epsilon(q, \omega)$ gives a convenient description (Quinn 1962, Howie and Stern 1972, Ritchie and Howie 1977). The mean free path is then given by the expression

$$\Lambda_{el}^{-1}(\theta_m) = \frac{2(V_0^i)_{el}}{\hbar v} = \frac{2e^2}{\pi\hbar v^2}\int_0^{E/\hbar} d\omega \int_{q(\theta_m)}^{q(\pi)} \frac{dq}{q} \operatorname{Im}\left\{-\frac{1}{\epsilon(q,\omega)}\right\} \tag{1}$$

where the integral over momentum transfer $\hbar q$ covers the whole range of scattering angle θ ($0 = \theta_m \leqslant \theta \leqslant \pi$) in LEED experiments where energy selection is used, but only the range outside $\theta_m \simeq 3$ mrad in normal electron microscopy work. Typical results for $\Lambda_{el}(0)$ are shown as a function of primary energy E in figure 1, and exhibit a broad minimum of about $\Lambda = 5$ Å for values of E around three times the threshold excitation energy of plasmons which make the dominant contribution to the effect. These data vary rather little from one material to another and are useful for discussing a wide

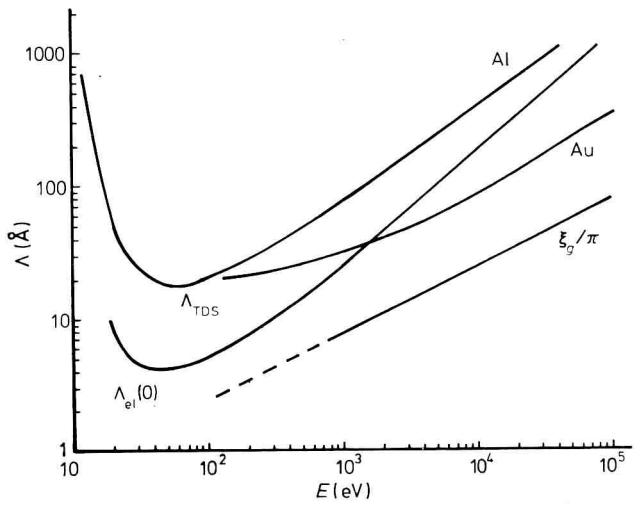

Figure 1. Mean free paths $\Lambda_{el}(0)$ and Λ_{TDS} (in Al and Au) shown approximately as functions of energy, together with the quantity ξ_g/π in a typical case.

range of inelastic scattering effects, including the surface sensitivity of LEED and RHEED and the escape depths of electrons generated in Auger spectroscopy or photoemission spectroscopy (e.g. Feuerbacher and Willis 1976). At low energies the results obtained from equation (1) agree quite closely with those of a more sophisticated calculation (Lundqvist 1969) which takes account of exchange effects. At high energies $\Lambda_{el}(0)$ tends to saturate (Ashley and Ritchie 1970).

The typical electron microscope objective aperture defines a scattering angle θ_m corresponding to a momentum transfer $\hbar q(\theta_m)$ which may approach the plasmon cut-off momentum $\hbar q_c$. Calculations of $\Lambda_{el}^{-1}(\theta_m)$ therefore require a dielectric constant which is adequate in this range of θ and incorporates both the valence-electron plasma modes and the single-electron excitations. Ritchie and Howie (1977) describe some presciptions for constructing suitable expressions for $\epsilon(q, \omega)$ based on either electron density data or optical data. For $\theta_m = 3$ mrad they quote values of $(V_0^i)_{el}$ ranging between 0·25 eV for Al and 0·51 eV for Au at 100 keV, which are much smaller than the values obtained previously using single-electron excitation theory (Whelan 1965, Radi 1970). Improved calculations of inelastic scattering processes are still required for a number of current aspects of electron microscopy such as weak-beam imaging and energy-loss micro-analysis.

The anomalous absorption parameter V_g^i arises mainly from thermal diffuse scattering (Whelan 1965, Hall and Hirsch 1965a, Kainuma and Yoshioka 1966, Humphreys and Hirsch 1968, Radi 1970). Hall and Hirsch obtained the results

$$V_{gh}^i = V_{g-h}^i = \frac{2\pi^2\hbar^3}{\Omega m_0^2 v} \int F_{gh}(S)\, S\, \mathrm{d}S\, \mathrm{d}\phi \tag{2}$$

$$F_{gh}(S) = f^*(|\mathbf{S} - \mathbf{g}|)\, f(|\mathbf{S} - \mathbf{h}|)[\exp(-M_{g-h}) - \exp(-M_{s-g} - M_{s-h})] \tag{3}$$

and so

$$\Lambda_{TDS}^{-1} = \frac{2(V_0^i)_{TDS}}{\hbar v} = \frac{8\pi^3\hbar^2}{\Omega m_0^2 v^2} \int_0^{2/\lambda} |f(S)|^2[1 - \exp(-2M_S)]\, S\, \mathrm{d}S \tag{4}$$

where Ω is the atomic volume, $S = 2 \sin\theta/\lambda$ and $M_S = \alpha S^2$ is the usual Debye–Waller term. The derivation assumed that the Born values f_B should be used for f in these calculations but this gives values of Λ_{TDS} which are much too small, not only at low energies (Howie and Stern 1972) but also at 100 keV in heavy elements (Badde and Reimer 1972). For such diffuse scattering calculations, where single atoms scatter independently, it would seem plausible to prefer the exact atomic scattering amplitude $f(S)$. Curves of Λ_{TDS} calculated on this assumption (Howie and Stern 1972) are shown in figure 1. In electron microscopy, where $\Lambda_{TDS} < \Lambda_{el}(\theta_m)$ in all but the lightest elements, and the parameter V_g^i is of paramount importance, thermal diffuse scattering is the most significant effect. In LEED however, though clearly less important, it usually seems to be ignored completely in practice. Contributions to V_0^i and V_g^i from thermal diffuse scattering have been estimated to lie in the range 0·1–1·0 eV for a number of elements at energies of 100, 500 and 1500 eV (Andersen and Howie 1975) so that perhaps it may not be altogether negligible. Equation (4) certainly implies that, if the Debye–Waller factor is regarded as necessary for dynamical calculations, the corresponding absorption effects ought also to be included.

Other small contributions to V_0^i and V_g^i may arise from weak beams (Gjønnes 1962, Hall and Hirsch 1965b) and from disorder scattering (Hall *et al* 1966, Howie and Stern 1972). It appears, however, that the current theory adequately explains the available experimental data, which are for the most part only semiquantitative.

For most work in high-energy electron diffraction the real part of the optical potential is adequately expressed in terms of the Born atomic scattering amplitudes multiplied by suitable Debye–Waller factors. The change in valence-electron distribution because of solid state binding effects is the main correction, and becomes significant in (for instance) critical-voltage experiments (§3). Additional contributions (Yoshioka 1957, Kainuma and Yoshioka 1966) arise from virtual excitation processes corresponding to the real excitation processes giving rise to absorption effects but the resulting increase in the inner potential (Ichikawa and Ohtsuki 1969) is less than 1 eV at high energies and probably too small to detect. Contributions from spin–orbit coupling are also probably very small but do not seem to have been calculated in detail.

The Debye–Waller factor $\exp(-M_g)$ arises if it is assumed that the elastic scattering is described by the static time-averaged part of the potential in the vibrating crystal. The difference between this approach and the correct procedure of taking the time average of the diffracted intensities in the vibrating crystal can be regarded as the virtual phonon contribution noted above. Exact dynamical theory calculations for vibrating crystals do not as yet exist. For the high-energy two-beam Laue case, however, it can be shown (see Appendix) that the Debye–Waller factor is valid for phonon wavelengths much less than the extinction distance but that long-wave phonons produce an opposite effect (i.e. they tend to increase V_g and therefore decrease the extinction distance as conjectured by Howie and Valdrè (1967)).

All of these difficulties are greatly increased in the LEED region. The quantity ξ_g/π calculated in the usual way can be regarded crudely as an amplitude mean free path for Bragg reflection and is indicated as a function of energy in figure 1. It is clear that at low energies strong diffraction effects can arise in a single layer of atoms, and that it is therefore better to give up the Born approximation and plane-wave expansions in favour of a more exact description of the scattering in each atomic core, based for example on phase-shift calculations (Pendry 1974). Exchange and correlation become important and different scattering models have then to be examined (Echenique and Titterington 1977). Contributions from virtual electronic excitations and phonons are also potentially very significant and it is not certain that they are adequately considered. For instance, the effects of phonons are apparently included via complex phase shifts calculated on the assumption of no correlation in the atomic vibrations (Holland 1971) – that is to say, in a very short wavelength limit. The effective extinction distance in LEED is so short that there must be many phonon modes which could produce quite different effects, as noted for high-energy electrons. Heine and Pendry (1969) drew attention to such phonons in LEED some years ago but no further calculations seem to have been made.

3. Bloch waves and dispersion surface concepts

Almost simultaneously with the first publication on the dynamical theory of electron diffraction (Bethe 1928), the foundations of solid state band theory were laid when

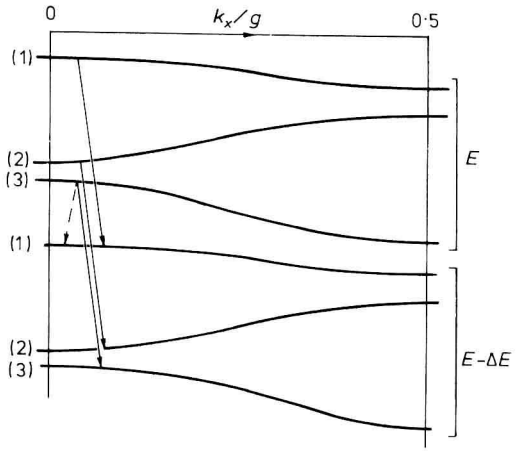

Figure 2. The first three branches of the high-energy dispersion surface in the systematic case for energies E and $E - \Delta E$. The three small-angle intraband inelastic transitions (shown by full arrows) all involve the same momentum transfer and energy loss and are hence induced by the same excitation, with consequent preservation of phase relations. The interband inelastic transition (broken arrow) is very weak.

Bloch (1929) investigated the wavefunctions of valence electrons in a periodic potential. Bloch waves and energy dispersion surfaces (figure 2) have also come to play a significant part in high-energy diffraction (for a review see Hirsch *et al* 1965). Typically they are computed in the projection approximation (Howie 1966, Berry 1971) involving two-dimensional Bloch waves which are usually described completely by a sum of plane waves or diffracted beams. Solutions involving up to several hundred plane waves can be computed when necessary but, in other cases of symmetry, quite useful analytical solutions with relatively small numbers of beams can be obtained (Hirsch *et al* 1965). The symmetry of electron diffraction effects has been discussed more generally using group theory (Buxton *et al* 1976, Kogiso and Takahashi 1977).

The apparent vanishing of the second-order Bragg reflection intensity and an associated reversal of Kikuchi-line contrast taking place at a sharply defined accelerating potential (Nagata and Fukuhara 1967, Watanabe *et al* 1968, 1969) is known in electron microscopy as the critical-voltage effect and constitutes a striking example of the usefulness of the dispersion surface concept. A rather crude explanation is that destructive interference occurs between single action of the second-order process measured (relativistically) by $V_{2g} \exp(-M_{2g})\, m/m_0$ and double action of the first-order process measured by $[V_g \exp(-M_g)\, m/m_0]^2$. More precisely, branches (2) and (3) of the dispersion surface (at the point $k_x = 0$ in figure 2) touch one another and exchange symmetry at the critical voltage (Metherell and Fisher 1969). The effect is very sensitive and has a number of applications (Lally *et al* 1972), including the precise measurement of scattering amplitudes (and hence electron distributions) in small samples of solids with an accuracy which can be a few parts per thousand and equals the best x-ray data (Swann *et al* 1974, Hewat and Humphreys 1974, Terasaki *et al* 1975). The critical-voltage effect in alloys has also been used to measure local changes in composition (Butler 1972) as well as Debye–Waller factors (Shirley *et al* 1975). Critical-voltage effects have also been observed for higher-order systematic reflections (Thomas 1972) and in high-symmetry orientations (Steeds *et al* 1975). Information about scattering amplitudes, Debye–Waller factors and vacancy concentrations in oxides has also been obtained by a study of the

influence of non-systematic many-beam effects on Kikuchi-line intersections (Gjønnes and Høier 1971, Høier and Andersson 1974, Watanabe *et al* 1974).

At voltages above the critical voltage in the systematic-diffraction case, the anomalous transmission effects change dramatically. They can, for instance, become good for incident beam directions parallel to the Bragg planes as a result of the symmetry interchange between branches (2) and (3) of the dispersion surface (Humphreys *et al* 1971). The detailed explanation of these effects must be regarded as a major success of dynamical theory.

Despite these recent successes of conventional plane-wave dynamical theory, there have been attempts to introduce cellular methods (e.g. Kambe *et al* 1974, Ozorio de Almeida 1975) using on the one hand some of the battery of concepts of valence band theory such as muffin-tin potentials, pseudopotentials, APW and KKR methods, etc which have been diffusing upwards in the energy scale via LEED, and on the other hand concepts of the classical channelling theory of particle motion in crystals (Gemmel 1974). For the systematic-diffraction or planar-channelling case, interesting connections can be drawn between quantities like the extinction distance and the wavelength of the trajectory oscillations of the particle in the channel (Howie 1968, Chadderton 1968, Howie *et al* 1970); it has also been possible to give a semiclassical treatment of the critical-voltage effect (Berry *et al* 1973, Buxton and Berry 1976).

However, it is in the two-dimensional cases of channelling along high-symmetry axes that these other methods are likely to be more economical than the conventional theory, since this can then involve several hundred beams. Kambe *et al* (1974) have identified some of the p- and d-type Bloch-wave states which are bound to the lines of atoms parallel to the axis with the classical rosette trajectories (Kreiner *et al* 1970) and the loosely bound s-type states (see also Gjønnes and Taftø 1976) with the classical 'weavon' trajectories (Nip *et al* 1968). The dependence of these axial channelling properties on accelerating potential can be directly observed in the electron microscope zone axis patterns (ZAPS) (Steeds *et al* 1975) and can be qualitatively accounted for by considering a simple integral of the projected potential. It is interesting to note, however, that in more recent quantitative studies of ZAPS and of the higher-order Laue zones visible in them (Jones *et al* 1977) the plane-wave expansion of the Bloch functions has again been used.

The Bloch wave concept is also useful in imperfect crystals. The effects of external fields or of a weak lattice distortion can be handled by a semiclassical theory of Bloch wave-packet propagation with a group velocity normal to the dispersion surface. So far this has proved more valuable in valence band theory and in x-ray topography than in electron diffraction, where it has been restricted to the external-field case. A uniform magnetic field B_y is equivalent (Jakubovics 1965, Wilkens 1965) to a lattice displacement $R_x = eB_y z^2/2\chi\hbar c = \alpha z^2/2g$. The semiclassical theory fails when interband scattering (or magnetic breakdown) occurs; by substituting for R in equation (A1) below it can be shown (Zener 1932) that the probability of this is $\exp(-\pi^2/\alpha\xi_g^2)$ and is negligible in practice. Interband scattering is important in most defect scattering problems; however, the Bloch wave model can be adapted to deal with this (Wilkens 1964) and the group-velocity concept has been useful in discussion of the validity of the column approximation (Howie and Basinski 1968).

The dispersion surface concept has also proved useful in discussing questions of small-

angle thermal diffuse scattering (Takagi 1958) or inelastic scattering such as plasmon excitation (Howie 1963). Various inelastic transitions can be depicted (figure 2). The absence of interband excitations and the preservation of the relative coherence between different Bloch waves means that good-quality diffraction contrast electron microscope images can often be observed using inelastically scattered electrons. Recently, Craven and Colliex (1977) have observed the 3·4 Å lattice image of graphite in the STEM using plasma-loss electrons. Although the theory has only been worked out in detail for crystals, it is almost certainly a widespread effect in electron microscopy. The observation of similar contrast effects in both zero-loss and energy-loss electrons does not imply, as is sometimes supposed, that the inelastic scattering process is localised, but rather that it is very delocalised (as indeed one must assume for the small momentum transfers involved in the excitation). The image contrast in both the zero-loss and the energy-loss electron images are generated by elastic scattering from the static potential in the specimen.

4. Coupled plane-wave diffraction theories

Despite the basic significance of the Bloch wave concept it has proved preferable for many purposes of practical computation (even in perfect crystals) to express the wavefunction as a sum of plane waves whose amplitudes depend on position rather than as a sum of Bloch waves. The coupled plane-wave approach (Takagi 1962) has many essentially similar formulations and its history can be traced from the earliest form of x-ray dynamical theory (Darwin 1914) through the work of Harding (1937) for the Bragg case, the work of Cowley and Moodie (1957) on Fourier images in transmission electron microscopy, the treatment of dislocation images by Howie and Whelan (1961) and the development of the so-called slice method for many-beam computations in perfect crystals (Goodman and Moodie 1974). Similar (though somewhat more complex) formulations have also been useful in LEED theory (Pendry 1974).

The computational advantages of the coupled plane-wave theories are particularly noticeable when large numbers of Bragg reflections are involved and when the integration distance is not too long (i.e. in rather thin or in heavily absorbing samples). The useful insight into scattering processes available in the Bloch wave picture is sacrificed in favour of an approach which is essentially simpler and more obviously related to the physics of the multiple-diffraction process, and better able to deal automatically with the complications which arise when Bloch waves can no longer be regarded as strictly independent, or when wave-matching has to be done at surfaces making arbitrary angles with the Bragg planes. To illustrate these points we outline here some of the applications to backscattering and x-ray production in crystals, since the use of plane-wave methods in transmission problems is covered elsewhere in these proceedings. Enhanced x-ray production and backscattering associated with electron waves concentrated at the atomic cores (Hirsch *et al* 1962) was first observed for fast electrons by Duncumb (1962) though noticed earlier for slow electrons by Laponsky and Whetton (1959) and interpreted kinematically (Soshea and Dekker 1961). Gemmell (1974) reviews the analogous classical blocking effect.

The x-ray production anomaly was further studied by Hall (1966), Miyake *et al* (1968). More recently Cherns *et al* (1973) showed that the so-called independent Bloch